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ous fruits but none that can be identified with accuracy.

A reference is also made in the manuscript to worms around the roots of peach trees which are said to cause an exudation of gum. This probably refers to the larvæ of some boring insect. An attempt was made to get rid of them by applying a handful of salt around the roots once or twice a season with the only result, however, that the larvæ were more numerous after the application than before.

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### SPECIAL ARTICLES

#### THE INVERSION OF MENTHONE BY SODIUM, POTASSIUM AND LITHIUM ETHYLATES, AND A METHOD OF ANALYSIS FOR MENTHONE IN PINE OILS

THE work of Tubandt<sup>1</sup> has shown that the reaction



can be followed polarimetrically, is monomolecular and is catalyzed by acids and bases. The present study has involved the measurement of the velocity of the inversion when brought about by sodium, potassium and lithium ethylates in absolute ethyl alcohol at 25°; a special constant temperature bath, holding silver-plated copper polarimeter tubes, has been employed.

The molar constant,  $K_N$ , found for the activity of the three ethylates at dilutions ranging from  $N/32$  to  $N/512$ , were substituted in the equation  $K_N = K_i\alpha + K_m(1 - \alpha)$ , derived by one of us<sup>2</sup> to express the activity of both the non-ionized molecules and the ions of a reacting electrolyte, and gave series of satisfactory constants for the activity of both the ethylate ions,  $K_i$ , and the non-ionized molecules  $K_m$ , of each ethylate.

It was found that the constant expressing the activity of the ethylate ion was the same, whether calculated from the data for sodium, potassium or lithium ethylate: for  $\text{NaOC}_2\text{H}_5$ ,  $K_i = 0.501$ ; for  $\text{KOC}_2\text{H}_5$ ,  $K_i = 0.501$ , and for  $\text{LiOC}_2\text{H}_5$ ,  $K_i = 0.496$ . The constants for

the reactivity of the non-ionized ethylate were found to be very nearly the same for sodium and potassium ethylates, but somewhat lower in the case of lithium ethylate, as has been found to occur with other reactions. Thus, for  $\text{NaOC}_2\text{H}_5$ ,  $K_m = 0.693$ ; for  $\text{KOC}_2\text{H}_5$ ,  $K_m = 0.701$ , and for  $\text{LiOC}_2\text{H}_5$ ,  $K_m = 0.478$ .

The relative magnitudes of these constants agree with the fact that the molar constant,  $K_N$ , drops off with dilution for sodium and potassium ethylates, but does not change with dilution in the case of lithium ethylate; that the molar constants for sodium and potassium ethylates are close to one another in value, but different from those for lithium ethylate; and, finally, that the reaction velocity constants become practically the same for all three ethylates in the very dilute solutions in which the metallic ethylate is nearly completely ionized.

Having shown above that sodium, potassium and lithium ethylates cause the inversion of menthone, it was thought important to use this as an analytical method to determine the presence of menthone, and its amount, in certain pine oils said to contain the levo form of this material. Eight per cent. absolute alcoholic solutions of pine oil and of several of its fractions were made. These contained also  $N/64$  sodium ethylate. These solutions showed no appreciable change in optical rotation in about three hours. In order to prove that no *l*-menthone was present in the pine oil an alcoholic solution containing 2 per cent. of partly inverted *l*-menthone and 8 per cent. of the same pine oil, or of its fractions, and  $N/64$  sodium ethylate, was found to give the usual change in rotation observed for alcoholic solutions of *l*-menthone. It is clear, then, that pine oils have no appreciable influence on the change of rotation of admixed *l*-menthone and that the amount and rapidity of change of rotation by a given concentration of sodium, potassium or lithium ethylate can be used as a measure of the amount of *d*- or *l*-menthone in pine oil in excess of any amount of the equilibrium mixture of *d*- and *l*-menthone. If there is an excess of *l*-menthone present its effect on the rotation may be offset by other constituents hav-

<sup>1</sup> *Ann.*, 339, 41, 1904.

<sup>2</sup> *Am. Chem. Jour.*, 48, 359, 1912.

ing an opposite rotation. For example, *l*-borneol acetate with a specific rotation of  $-44.4^\circ$  could yield ethyl acetate and borneol with a specific rotation of  $-37.8^\circ$  *l*-menthol acetate, with a specific rotation of  $-79.4^\circ$ , yields *l*-menthol having a specific rotation of  $-50^\circ$ . The change of rotation in these two cases is in the same direction as that of *l*-menthone and would be added to it. In other cases, however, the changes might be in the opposite direction. The change in rotation due to the borneol acetate, for example, can be calculated from the ester number, which is always determined, and the proper correction can be made.

The same idea can be applied to the calculation of the amounts of each of two esters whose identities are known and whose changes of rotation by sodium ethylate are different or of opposite sign. The ester number and change of rotation will give the amount of each. When the mixtures become complex the "unknowns" become too large and the method becomes only qualitative at best.

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#### MEASURING BIOLOGICAL ACTIONS BY THE FREEZING-POINT METHOD DIRECTLY IN THE SOIL

It has already been shown that the freezing-point method can be employed to measure (a) the concentration of the plant-cell sap directly in the plant tissue,<sup>1</sup> (b) the concentration of the soil solution at different moisture contents, directly in the soil,<sup>2</sup> and (c) the effect of application of soluble chemical compounds upon the soil solution.<sup>2</sup> In the present note it is desired to announce that the freezing-point method can be used also to study biological activities, by measuring the products of decomposition of organic materials, directly in the soil.

In conjunction with the experiments on the effect of the application of soluble chemical compounds upon the concentration of the soil

solution, the effect of the decomposition of various nitrogenous substances was also studied. It has been found that the products of decomposition of these nitrogenous substances increased markedly the concentration of the soil solution, and the magnitude of the increase varied with the nature of the compound and amount employed. In the following table there are presented the results of a single experiment which might serve to typify the character of the general data obtained. This experiment consisted of mixing 0.5 and 1.0 grams of dried blood, cotton-seed meal and animal tankage with 800 grams of soil (equivalent to about 1,250 and 2,500 pounds per 2,000,000 pounds of soil respectively), allowing the mixture to stand in room temperature for five weeks at optimum moisture content and then determining the freezing-point depression, according to the method already described in Tech. Bull. No. 24 of this Station. The percentage of nitrogen contained by the materials is as follows: dry blood, 14.14 per cent.; cotton-seed meal, 7 per cent., and animal tankage, 10 per cent.

TABLE I

*Effect of Decomposition of Nitrogenous Substances Upon the Freezing-Point Depression of the Soil Solution*

Substance	Grs.	Depression Due to Substance
Dry blood .....	0.5	.025° C.
" " .....	1.0	.050°
Animal tankage ...	0.5	.020°
" " ...	1.0	.040°
Cotton-seed meal ...	0.5	.017°
" " " ..	1.0	.030°

The depression in every case is the difference between the depression of the untreated soil or check and that of the treated. In other words, the check was used as a standard.

It will be seen then that the decomposition of these nitrogenous materials increased the depression, and hence the concentration of the soil solution, markedly, and the magnitude of the increase seems to vary with the nature of the material and quantity employed.

In some other experiments the amounts of these nitrogenous materials were used, not in equivalent weight but in equivalent nitrogen content and the freezing-point depression was

<sup>1</sup> *J. Am. Soc. Agr.*, Vol. 8, No. 1, 1916.

<sup>2</sup> Tech. Bull. No. 24, Mich. Expt. Sta., 1916.